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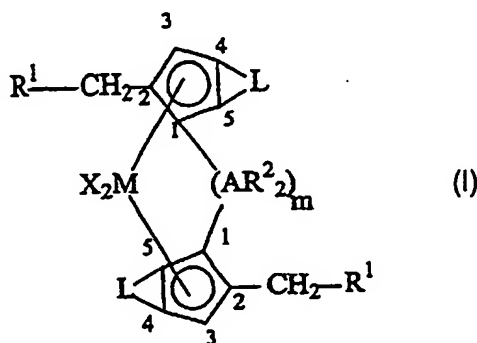
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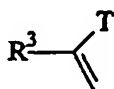
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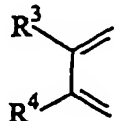
(54) Title: PROCESS FOR THE POLYMERIZATION OF 1-BUTENE



(57) Abstract: A process for polymerizing 1-butene comprising the step of contacting under polymerization conditions 1-butene and optionally from 0 to 20% by mol of an alpha olefin with a catalyst system obtainable by contacting a bridged metallocene compound of formula (I) wherein R<sup>1</sup> and R<sup>2</sup> are an hydrocarbon radical A is a carbon atom, a germanium atom or a silicon atom; m is 1, 2; M is a metal of group 4 of the Periodic Table of the Elements; X, is hydrogen, a halogen atom, or a group R, OR, OSO<sub>2</sub>CF<sub>3</sub>, OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub>, wherein the substituents R are hydrocarbon radical; L is a moiety of formula (IIa) or (IIb) wherein T is an oxygen (O) or sulphur (S) atom or a CH<sub>2</sub> group; and R<sup>3</sup> and R<sup>4</sup> are hydrogen atoms or hydrocarbon radicals; one or more alumoxanes or compounds able to form an alkylmetallocene cation; and optionally an organo aluminium compound.



(IIa)



(IIb)

WO 02/100908 A1

## PROCESS FOR THE POLYMERIZATION OF 1-BUTENE

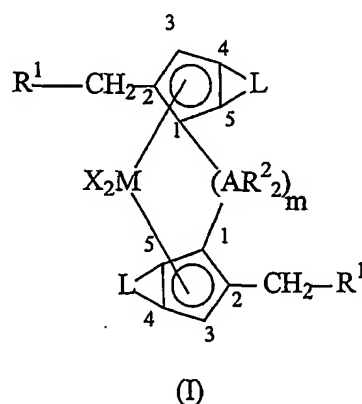
The present invention relates to a process for polymerizing 1-butene by using a substituted bis cyclopentadienyl bridged metallocene compound. 1-butene polymers are well known in the art. In view of their good properties in terms of pressure resistance, creep resistance, and impact strength they have a lot of uses such as the manufacture of pipes to be used in the metal pipe replacement, easy-open packaging and films. The 1-butene (co)polymers are generally prepared by polymerizing 1-butene in the presence of  $\text{TiCl}_3$  based catalysts components together with diethylaluminum chloride (DEAC) as cocatalyst. In some cases diethyl aluminum iodide (DEAI) is also used in mixtures with DEAC. The polymers obtained, however, generally do not show satisfactory mechanical properties. Furthermore, in view of the low yields obtainable with the  $\text{TiCl}_3$  based catalysts, the 1-butene polymers prepared with these catalysts have a high content of catalyst residues (generally more than 300 ppm of Ti) which lowers the properties of the polymers making it necessary a deashing step. 1-butene (co)polymers can also be obtained by polymerizing the monomers in the presence of a stereospecific catalyst comprising (A) a solid component comprising a Ti compound and an electron-donor compound supported on  $\text{MgCl}_2$ ; (B) an alkylaluminum compound and, optionally, (C) an external electron-donor compound. A process of this type is disclosed in EP-A-172961 and more recently in WO99/45043.

In *Macromolecules* 1995, 28, 1739-1749 *rac*-dimethylsilylbis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride and methylaluminoxane have been used for polymerizing 1-butene, even if the yield of the process is not indicated the molecular weight of the polymer ( $M_n$ ) is very low. Recently metallocene compounds have been used for producing 1-butene polymers. In *Macromol. Rapid Commun.* 18, 581-589 (1997) *rac* and *meso*-[dimethylsilylenebis(2,3,5-trimethyl-cyclopentadienyl)]zirconium dichloride have been used for the polymerization of 1-butene, the yields of the process and the molecular weight of the obtained polymers are rather low. More recently in *Macromolecules* 2000, 33, 1955-1956  $\text{Me}_2\text{Si}(2\text{-Me-4,5-BzoInd})_2\text{ZrCl}_2$ ,  $\text{Me}_2\text{Si}(2\text{-Me-4-PhInd})_2\text{ZrCl}_2$  and  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  have been tested in the polymerization of 1-butene. Even if the molecular weights of the polymers appear to be quite high, the activities of these catalysts are low as shown in the comparative examples of the present application.

A new process that permits to obtain 1-butene polymer with high molecular weight and in high yield is therefore desirable.

An object of the present invention is a process for polymerizing 1-butene comprising the step of contacting under polymerization conditions 1-butene and optionally from 0 to 20% by mol, preferably from 0 to 10% by mol of ethylene, propylene and/or an alpha olefin of formula  $\text{CH}_2=\text{CHZ}$  wherein Z is a  $\text{C}_3\text{-C}_{10}$  alkyl group, in the presence of a catalyst system obtainable by contacting:

- a) a racemic or racemic-like bridged metallocene compound of formula (I)



wherein

$\text{R}^1$ , same or different, are selected from the group consisting of hydrogen, a linear or branched saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl,  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $\text{R}^1$  is hydrogen or a  $\text{C}_1\text{-C}_{20}$ -alkyl radical, more preferably  $\text{R}^1$  is hydrogen, methyl or ethyl;

A, same or different, is a carbon atom, a germanium atom or a silicon atom; with the proviso that, when m is 1, A is different from a carbon atom; preferably A is a silicon atom;

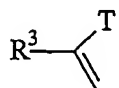
m is 1 or 2, preferably m is 1;

$\text{R}^2$ , same or different, is hydrogen, a linear or branched saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl,  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $\text{R}^2$  is hydrogen a  $\text{C}_1\text{-C}_{20}$ -alkyl or a  $\text{C}_6\text{-C}_{20}$ -aryl; more preferably  $\text{R}^2$  is hydrogen, methyl or phenyl;

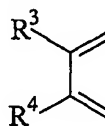
M is a transition metal atom selected from those belonging to group 4 of the Periodic

Table of the Elements (new IUPAC version); preferably M is zirconium or hafnium, more preferably M is zirconium; X, same or different, is a hydrogen atom, a halogen atom, or a R, OR, OSO<sub>2</sub>CF<sub>3</sub>, OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub> group, wherein R is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>7</sub>-C<sub>20</sub> alkylaryl or C<sub>7</sub>-C<sub>20</sub> arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR<sup>11</sup>O group wherein R<sup>11</sup> is a divalent radical selected from C<sub>1</sub>-C<sub>20</sub> alkylidene, C<sub>6</sub>-C<sub>40</sub> arylidene, C<sub>7</sub>-C<sub>40</sub> alkylarylidene and C<sub>7</sub>-C<sub>40</sub> arylalkylidene radicals; preferably X is a hydrogen atom, a halogen atom or a R group; more preferably X is chlorine or a methyl radical;

L, same or different, is a moiety of formula (IIa) or (IIb):



(IIa)



(IIb)

wherein

in the moiety of formula (IIa) T bonds to the cyclopentadienyl group in position 5;

T is an oxygen (O) atom, a sulphur (S) atom or a CH<sub>2</sub> group; preferably T is sulphur;

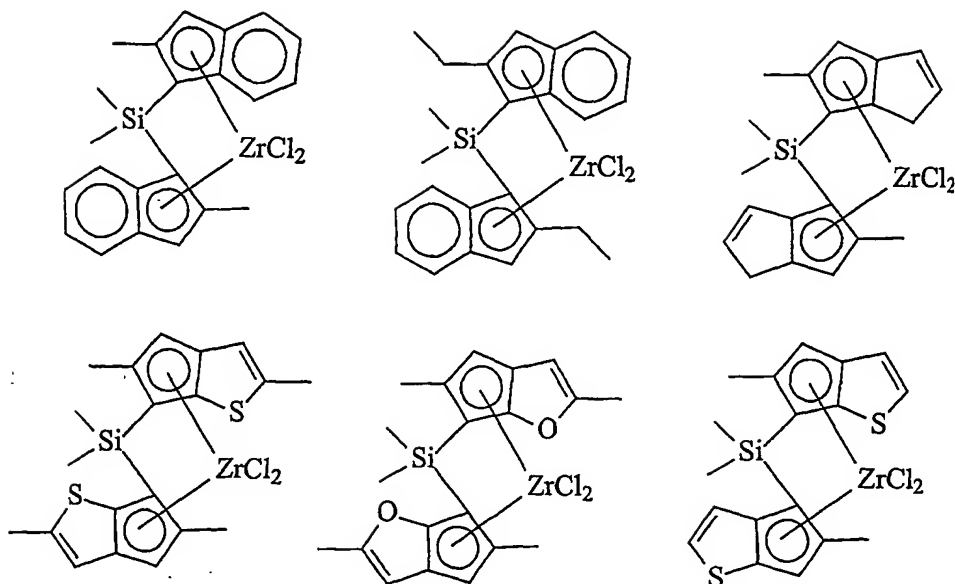
R<sup>3</sup> and R<sup>4</sup>, same or different, are hydrogen, linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or in the moiety (IIb) R<sup>3</sup> and R<sup>4</sup> form together a saturated or unsaturated, condensed 5 or 6 membered ring optionally containing heteroatoms belonging to groups 13-16 of the Periodic Table of the Elements; preferably, in the moiety of formula (IIa) R<sup>3</sup> is hydrogen or methyl;

preferably in the moiety of formula (IIb) R<sup>3</sup> and R<sup>4</sup> are hydrogen or methyl;

- b) an alumoxane or a compound able to form an alkylmetallocene cation; and
- c) optionally an organo aluminum compound.

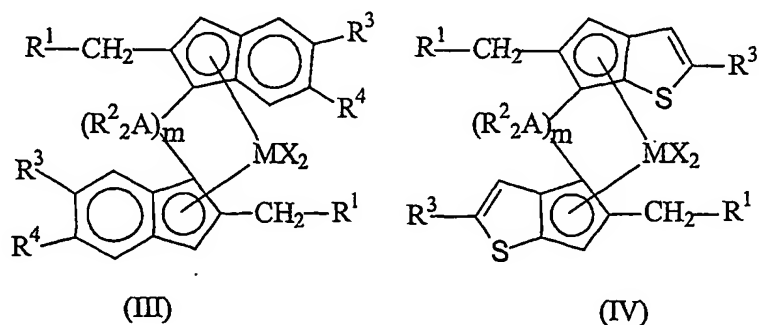
Preferred structures for the (R<sup>2</sup><sub>2</sub>A)<sub>m</sub> bridging group are Si(CH<sub>3</sub>)<sub>2</sub>, SiPh<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, the Si(CH<sub>3</sub>)<sub>2</sub> being the most preferred.

Non limitative examples of compound of formula (I) are:



as well as the corresponding dihydride and dimethyl compounds.

Preferred compounds of formula (I) are those of formulas (III) or (IV):



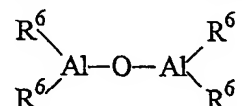
wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , A, M, X and m are defined as above.

Metallocene compounds of formula (I) are well known in the art, they can be prepared according to known procedure, such as those described in USP 5,145,819, EP-A-0 485 823, WO 98/22486 and WO 01/44318.

Alumoxanes used as component b) can be obtained by reacting water with an organo-aluminium compound of formula  $H_jAlR^{6}_{3-j}$  or  $H_jAl_2R^{6}_{6-j}$ , where  $R^6$  substituents, same or different, are hydrogen atoms,  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cyclalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl or  $C_7$ - $C_{20}$ -arylalkyl, optionally containing silicon or germanium atoms with the proviso that at least one  $R^6$  is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and

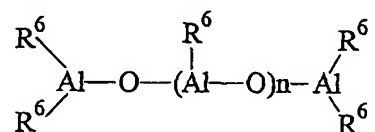
100:1. The molar ratio between aluminium and the metal of the metallocene is comprised between about 10:1 and about 20000:1, and more preferably between about 100:1 and about 5000:1.

The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

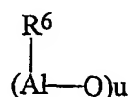


wherein the substituents  $\text{R}^6$ , same or different, are described above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein  $n$  is 0 or an integer from 1 to 40 and the substituents  $\text{R}^6$  are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein  $u$  is an integer from 2 to 40 and the  $\text{R}^6$  substituents are defined as above. Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO). Particularly interesting cocatalysts are those described in WO 99/21899 and in PCT/EP00/09111 in which the alkyl and aryl groups have specific branched patterns. Non-limiting examples of aluminium compounds according to said international applications are:

tris(2,3,3-trimethyl-butyl)aluminium, tris(2,3-dimethyl-hexyl)aluminium, tris(2,3-dimethyl-butyl)aluminium, tris(2,3-dimethyl-pentyl)aluminium, tris(2,3-dimethyl-heptyl)aluminium, tris(2-methyl-3-ethyl-pentyl)aluminium, tris(2-methyl-3-ethyl-hexyl)aluminium, tris(2-methyl-3-ethyl-heptyl)aluminium, tris(2-methyl-3-propyl-hexyl)aluminium, tris(2-ethyl-3-methyl-butyl)aluminium, tris(2-ethyl-3-methyl-pentyl)aluminium, tris(2,3-diethyl-pentyl)aluminium, tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethyl-pentyl)aluminium,

tris(2,3,3-trimethyl-hexyl)aluminium, tris(2-ethyl-3,3-dimethyl-butyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-dimethyl-butyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-phenyl-butyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-3-phenyl-butyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-phenyl)-propyl]aluminium, tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium, tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl]aluminium and tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of formula  $D^+E^-$ , wherein  $D^+$  is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and  $E^-$  is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic monomer. Preferably, the anion  $E^-$  comprises of one or more boron atoms. More preferably, the anion  $E^-$  is an anion of the formula  $BAR_4^{(-)}$ , wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred examples of these compounds are described in WO 91/02012. Moreover, compounds of the formula  $BAR_3$  can conveniently be used. Compounds of this type are described, for example, in the published International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula  $BAR_3P$  wherein P is a substituted or unsubstituted pyrrol radicals. These compounds are described in WO 01/62764. all these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2:1; more preferably about 1:1.

Non limiting examples of compounds of formula  $D^+E^-$  are:

Triethylammoniumtetra(phenyl)borate,

Tributylammoniumtetra(phenyl)borate,  
 Trimethylammoniumtetra(tolyl)borate,  
 Tributylammoniumtetra(tolyl)borate,  
 Tributylammoniumtetra(pentafluorophenyl)borate,  
 Tributylammoniumtetra(pentafluorophenyl)aluminate,  
 Tripropylammoniumtetra(dimethylphenyl)borate,  
 Tributylammoniumtetra(trifluoromethylphenyl)borate,  
 Tributylammoniumtetra(4-fluorophenyl)borate,  
 N,N-Dimethylaniliniumtetra(phenyl)borate,  
 N,N-Diethylaniliniumtetra(phenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,  
 Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,  
 Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,  
 Triphenylphosphoniumtetrakis(phenyl)borate,  
 Triethylphosphoniumtetrakis(phenyl)borate,  
 Diphenylphosphoniumtetrakis(phenyl)borate,  
 Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,  
 Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,  
 Triphenylcarbeniumtetrakis(phenyl)aluminate,  
 Ferroceniumtetrakis(pentafluorophenyl)borate,  
 Ferroceniumtetrakis(pentafluorophenyl)aluminate.  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate.

Further compounds that can be used are those of formula  $RM'-O-M'R$ , R being an alkyl or aryl group, and M' is selected from an element of the Group 13 of the Periodic Table of the Elements (new IUPAC version). Compounds of this type are described, for example, in the International patent application WO 99/40129. Organic aluminum compounds used as compound c) are those of formula  $H_jAlR^6_{3-j}$  or  $H_jAl_2R^6_{6-j}$  described above. The polymerization process of the present invention can be carried out in liquid phase, optionally



in the presence of an inert hydrocarbon solvent, or in gas phase. Said hydrocarbon solvent can be either aromatic (such as toluene) or aliphatic (such as propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane). Preferably the polymerization is carried out in liquid monomer. The polymerization temperature preferably ranges from 0°C to 250°C; preferably comprised between 20°C and 150°C and, more particularly between 40°C and 90°C; Generally, the polymers of the present invention are endowed with a narrow molecular weight distribution. The molecular weight distribution is represented by the ratio  $M_w/M_n$  which, for the polymers of the present invention, when the metallocene used is a pure isomer, is generally lower than 3, preferably lower than 2.5. The molecular weight distribution can be varied by using mixtures of different metallocene compounds or mixtures of the metallocene compound of formula (I) and a Ziegler-Natta catalyst or by carrying out the polymerization in several stages at different polymerization temperatures and/or different concentrations of the molecular weight regulators and/or different monomer concentration. The polymerization yield depends on the purity of the transition metal organometallic catalyst compound a) in the catalyst, therefore, said compound can be used as such or can be subjected to purification treatments before use. With the process of the present invention 1-butene can be polymerized with high yields and the isotactic polymers obtained show a high molecular weight and a low content of regioerrors, i.e. 4,1 insertions. Therefore another object of the present invention is a 1-butene homopolymer having the following characteristics:

- intrinsic viscosity (I.V.) > 1 dL/g; preferably >1.1 dL/g
- molecular weight distribution ( $M_w/M_n$ ) <3; preferably <2.5;
- isotactic triads (mm) > syndiotactic triads (rr); preferably isotactic triads (mm) >97%; more preferably >98%; and
- 4,1 insertions < 0.35%; preferably <0.3%; more preferably <0.25%.

Preferably the 1-butene homopolymer shows the presence of 4,1 insertions i.e. 4,1 insertions are > 0; more preferably the 4,1 insertions are > 0.05%; even more preferably > 0.1%.

With the process of the present invention it is possible to obtain a plastomeric 1-butene homopolymer. Thus further object of the present invention is a 1-butene homopolymer having the following characteristics:

- intrinsic viscosity (I.V.) > 1 dL/g; preferably >1.1 dL/g;
- flexural modulus (ASTM D 638) < 200%; preferably <190%;
- 4,1 insertions < 0.35%; preferably <0.30%; more preferably < 0.25%.

Preferably the 1-butene homopolymer shows the presence of 4,1 insertions i.e. 4,1 insertions are  $> 0$ ; more preferably the 4,1 insertions are  $> 0.01\%$ .

Said elastomeric 1-butene homopolymer is further endowed with a yield strength (ASTM D 638)  $> 8$  MPa; preferably comprised between 8 MPa and 15 MPa.

Said elastomeric 1-butene homopolymer is further endowed with a break strength (ASTM D 638)  $> 20$  MPa; preferably comprised between 20 MPa and 35 MPa.

Said elastomeric 1-butene homopolymer is further endowed with elongation at break (ASTM D 638)  $> 390\%$ ; preferably  $> 400\%$ .

When 1-butene is copolymerized with ethylene, propylene or an  $\alpha$  olefin of formula  $\text{CH}_2=\text{CHZ}$  wherein Z is a  $\text{C}_3\text{-C}_{10}$  alkyl group a copolymer having a comonomer derived unit content from 0.01 to 50% by weight can be obtained, preferably from 0.5 to 20% by weight. Preferred comonomers are ethylene or propylene.

The following examples are given to illustrate and not to limit the invention.

#### Experimental section

The intrinsic viscosity (I.V.) was measured in tetrahydronaphthalene (THN) at  $135^\circ$ .

The melting points of the polymers ( $T_m$ ) were measured by Differential Scanning Calorimetry (D.S.C.) on a Perkin Elmer DSC-7 instrument, according to the standard method. A weighted sample (5-10 mg) obtained from the polymerization was sealed into aluminum pans and heated at  $180^\circ\text{C}$  with a scanning speed corresponding to  $10^\circ\text{C}/\text{minute}$ . The sample was kept at  $180^\circ\text{C}$  for 5 minutes to allow a complete melting of all the crystallites. Successively, after cooling to  $20^\circ\text{C}$  with a scanning speed corresponding to  $10^\circ\text{C}/\text{minute}$ . After standing 2 minutes at  $20^\circ\text{C}$ , the sample was heated for the second time at  $180^\circ\text{C}$  with a scanning speed corresponding to  $10^\circ\text{C}/\text{min}$ . In this second heating run, the peak temperature was taken as the melting temperature ( $T_m$ ) and the area as global melting enthalpy ( $\Delta H_f$ ).

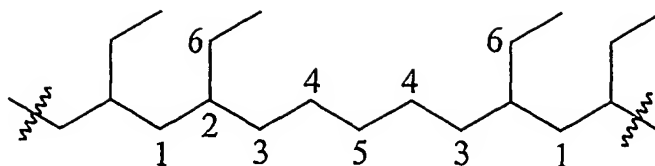
The molecular weight distribution was determined on a WATERS 150 C using the following chromatographic conditions:

Columns:	3x SHODEX AT 806 MS; 1x SHODEX UT 807; 1x SHODEX AT-G;
Solvent:	1,2,4 trichlorobenzene (+ 0.025% 2,6-Di-tert-Butyl-4-Methyl-Phenol);
Flow rate:	0.6 - 1 ml/min;
Temperature:	$135^\circ\text{C}$ ;
Detector:	INFRARED AT $\lambda \approx 3.5\mu\text{m}$ ;
Calibration:	Universal Calibration with PS-Standards.

$^{13}\text{C}$ -NMR spectra were acquired on a DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode at 120 °C. The peak of the  $2\text{B}_2$  carbon (nomenclature according to Carman, C. J.; Harrington, R. A.; Wilkes, C. E. *Macromolecules* 1977, 10, 535) was used as internal reference at 27.73. The samples were dissolved in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 120 °C with a 8% wt/v concentration. Each spectrum was acquired with a 90° pulse, 15 seconds of delay between pulses and CPD (waltz16) to remove  $^1\text{H}$ - $^{13}\text{C}$  coupling. About 3000 transients were stored in 32K data points using a spectral window of 6000 Hz. Assignments of 4,1 insertion were made according to Busico (V. Busico, R. Cipullo, A. Borriello, *Macromol. Rapid. Commun.* 1995, 16, 269-274)

Chemical Shift (ppm)	Carbon	Sequence
40.21	$\text{CH}_2$ ( $\text{S}_{\alpha\alpha}$ )	B
39.65	$\text{CH}_2$	D1
37.3	CH	D2
34.99	CH	B
34.31	$\text{CH}_2$	D3
31.13	$\text{CH}_2$	D5
27.73	$\text{CH}_2$ branch	B mmmm
27.57	$\text{CH}_2$ branch	B mmmr
27.37	$\text{CH}_2$ branch	B mmrr
27.21-27.14	$\text{CH}_2$	D4+D6
26.57	$\text{CH}_2$ branch	B mrrm
10.96	$\text{CH}_3$	B

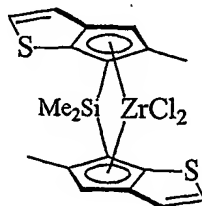
The content of 4,1 insertions was calculated as follows: 4,1 units =  $0.5 \times I_4 \times 100 / (I_2 + I_4)$



4,1-sequence (D)

**Preparation of catalyst components**

rac dimethylsilylbis(2-methyl-indenyl) zirconium dichloride (A-1) was prepared according to USP 5,145,819. rac dimethylsilylbis(2-methyl-4-phenyl-indenyl) zirconium dichloride (A-2) was prepared according to USP 5,786,432. rac dimethylsilylbis(2-methyl-4, 5 benzo-indenyl) zirconium dichloride (A-3) was prepared according to USP 5,830,821. rac dimethylsilylbis(indenyl) zirconium dichloride (A-4) was prepared according to USP 5,616,747. Dimethylsilylbis bis(2-methyl-cyclopento[2,3-b]thiophen-6-yl) zirconium dichloride [A5]



was prepared according to WO 98/22486.

The cocatalyst methylalumoxane (MAO) was a commercial product which was used as received (Witco AG, 10 %wt/vol toluene solution, 1.7 M in Al).

**Example 1 and comparative examples 2-3 1-butene homopolymer**

The catalyst mixture was prepared by dissolving the amount of the metallocene indicated in table 1 in 8 ml of toluene with the proper amount of the MAO solution (amounts are reported in table 1), obtaining a solution which was stirred for 10 min at room temperature before being injected into the autoclave. 4 mmol of Al(*i*-Bu)<sub>3</sub> (TIBA) (as a 1 M solution in hexane) and 712 g of 1-butene were charged, at room temperature, in a 2.3-L jacketed stainless-steel autoclave, equipped with magnetically driven stirrer and a 35-mL stainless-steel vial, connected to a thermostat for temperature control. The autoclave was then thermostatted at 58°C and the catalyst system, prepared as reported above, was injected in the autoclave by means of nitrogen pressure through the stainless-steel vial. The temperature was rapidly raised to 60°C and the polymerization was carried out at constant temperature, for the time indicated in table 1. After cooling the reactor to room temperature, the polymer was dried

under reduced pressure, at 60 °C. The polymerization conditions and the characterization data of the obtained polymers are reported in Table 1.

#### **Comparative example 4     1-butene homopolymer**

The catalyst system was prepared by dissolving 2.2 mg of metallocene A-4 in 22 ml of toluene and then adding 9.42 mmol of MAO ( $Al/Zr = 1930$ ). The obtained solution was stirred for 10 minutes at room temperature, before being injected into the autoclave. 4 mmol of  $Al(i-Bu)_3$  (TIBA) (as a 1 M solution in hexane) and 560 g of 1-butene were charged, at room temperature, in a 2.3-L jacketed stainless-steel autoclave, equipped with magnetically driven stirrer and a 35-mL stainless-steel vial, connected to a thermostat for temperature control. The autoclave was then thermostatted at 48°C and the catalyst system, prepared as reported above, was injected in the autoclave by means of nitrogen pressure through the stainless-steel vial. The temperature was rapidly raised to 50°C and the polymerization was carried out at constant temperature, for 60 minutes. After cooling the reactor to room temperature, the polymer was dried under reduced pressure, at 60 °C. The polymerization conditions and the characterization data of the obtained polymers are reported in Table 1.

#### **Examples 5-9             1-butene homopolymer**

The catalyst mixture was prepared by dissolving the amount of the metallocene indicated in table 2 in toluene with the proper amount of the MAO solution (amounts are reported in table 2  $Al/Zr = 1000$ ), obtaining a solution which was stirred for 10 min at room temperature before being injected into the autoclave.

A 4.25 litres steel autoclave, equipped with magnetically stirred anchor (usual stirring rate 550 rpm) and with different Flow Record & Control systems (FRC), among which a FRC having maximum flow rate of 9000 gr/hour for 1-butene and two FRC having maximum flow rate of 500 and 30 g/h for ethylene is cleaned with warm nitrogen (1.5 barg  $N_2$ , 70°C, 1 hour). After the above mentioned autoclave cleaning, the stirring starts and 1-butene is fed into the reactor (1350 gr at 30°C) together with 6 mmol of  $Al(i-Bu)_3$  (TIBA) (as a 1 M solution in hexane). Subsequently, the reactor inner temperature is raised from 30°C to the polymerisation temperature (indicated in table 2); as a consequence the pressure increases. When pressure and temperature are constant, the catalytic solution is fed into the reactor with a nitrogen overpressure. The polymerisation is run for a time indicated in table 2 at the chosen polymerization temperature. Then the stirring is interrupted; the pressure into the autoclave is raised to 20 bar-g with nitrogen. The bottom discharge valve is opened and the 1-butene/poly-1-

butene mixture is discharged into the steel heated tank containing water at 70°C. The tank heating is switched off and a flux of 0.5 bar-g nitrogen is fed. After 1 hour cooling at room temperature the steel tank is opened and the wet polymer collected. The wet polymer is dried in a oven under nitrogen at 70°C. The polymerization conditions and the characterization data of the obtained polymers are reported in Table 2. The polymer obtained in example 8 was further analyzed by NMR according to the procedure described above. The sample shows the presence of 4,1 insertions.

#### **Characterization of homopolymer**

Samples of polymer obtained from examples 8 and 9 were ground in an electric mill with liquid nitrogen in order to achieve the right size to feed them in a Brabender® mixer chamber. The ground samples were mixed in a Brabender® chamber with 1% 2,6-di-*t*-butyl-4-methyl phenol (BHT) at 200°C and then transformed in 1.9 and 4.0 mm thick plaques through compression molding at 200°C. The 1.9 mm thick plaques were submitted to tensile test (according to ASTM D 638 method), while the 4.0 mm thick plaques were submitted to the flexural modulus determination according to ISO 178 method. The results are reported in table 2a.

#### **Examples 10-13 1-butene/ethylene copolymer**

The catalyst mixture was prepared by dissolving the amount of the metallocene indicated in table 2 in toluene with the proper amount of the MAO solution (amounts are reported in table 3 Al/Zr = 500 excepting for example 10 when Al/Zr is 1000), obtaining a solution which was stirred for 10 min at room temperature before being injected into the autoclave. A 4.25 litres steel autoclave, equipped with magnetically stirred anchor (usual stirring rate 550 rpm) and with different Flow Record & Control systems (FRC), among which a FRC having maximum flow rate of 9000 gr/hour for 1-butene and two FRC having maximum flow rate of 500 and 30 g/h for ethylene is cleaned with warm nitrogen (1.5 barg N<sub>2</sub>, 70°C, 1 hour). After the above mentioned autoclave cleaning, the stirring starts, 1-butene is fed into the reactor (1350 gr at 30°C excepting for example 10 wherein 1368 g of 1-butene are used) with the amount of ethylene reported in table 3, together with 6 mmol of Al(*i*-Bu)<sub>3</sub> (TIBA) (as a 1 M solution in hexane). Subsequently, the reactor inner temperature is raised from 30°C to the polymerisation temperature (indicated in table 3); as a consequence the pressure increases. When pressure and temperature are constant, the catalytic solution is fed into the reactor with a nitrogen overpressure and the polymerisation pressure is kept constant feeding only

ethylene (amount indicated in table 3). The polymerisation is run for a time indicated in table 3 at the chosen polymerization temperature. Then the stirring is interrupted; the pressure into the autoclave is raised to 20 bar-g with nitrogen. The bottom discharge valve is opened and the 1-butene/poly-1-butene mixture is discharged into the steel heated tank containing water at 70°C. The tank heating is switched off and a flux of 0.5 bar-g nitrogen is fed. After 1 hour cooling at room temperature the steel tank is opened and the wet polymer collected. The wet polymer is dried in a oven under nitrogen at 70°C. The polymerization conditions and the characterization data of the obtained polymers are reported in Table 3

Table 1

Ex	met.	mg	mmol Al	Al/Zr	t (min)	yield (g)	Activity kg/(g <sub>cat</sub> *h)	I.V.	Triads mm %	regioerrors % (4,1 insertions)	T <sub>m</sub> (II) °C	ΔH <sub>f</sub> J/g	Mw/Mn
1	A-1	4	8.39	1000	15	64.7	129.4	1.2	98.5	0.2	100	32.1	2.16
2*	A-2	4	6.36	1000	60	39.5	9.9	0.9	≈100	0.4	n.a.	33	n.a.
3*	A-3	4	6.36	1000	60	17.5	4.4	1.1	99.2.	1	n.a.	n.a.	2.7
4*	A-4	2.2	9.42	1930	60	161	73.2	0.2	n.a.	n.a.	97	45	n.a.

\*comparative

n.a. = not available

Table 2

Ex	met.	mg	mmol Al	T <sub>pol</sub> °C	t (min)	yield (g)	Activity kg/(g <sub>cat</sub> *h)	I.V.	T <sub>m</sub> (II) °C	ΔH <sub>f</sub> J/g	Mw/Mn
5	A-1	3.9	8.28	50	120	150	19.2	2.23	104	27.8	2.19
6	A-1	2	4.20	75	60	45	22.5	1.13	93	28.9	2.23
7	A-1	2	4.20	85	60	187	93.5	1.28	97	28.3	2.27
8	A-5	2	4.08	50	60	185	92.5	2.15	90	19.6	2.15
9	A-5	2	4.08	70	60	320	160	1.04	85	15.1	2.34

Table 2a

Ex	Flexural modulus (MPa)	Yield strength (MPa)	Break strength (MPa)	Elongat. at break (%)
8	160	10.2.	30.6	420
9	187	9.1	24.1	480



Table 3

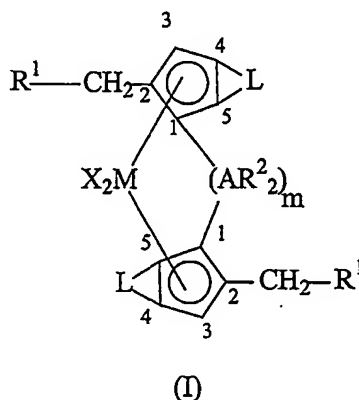
Ex	met.	mg	mmol Al	T <sub>pol</sub> °C	t (min)	C <sub>2</sub> added g	C <sub>2</sub> feed G	yield (g)	Activity kg/(g <sub>cat</sub> h)	I.V.	C <sub>2</sub> wt% (IR)	Mw/Mn
10	A-1	1	2.12	70	60	32	0	52.7	52.7	1.13	28.90	2.17
11	A-1	2	2.12	70	70	1	5.1	225	96.4	1.46	2.30	2.23
12	A-1	2	2.12	70	70	4	11.6	157	67.3	1.45	4.20	2.16
13	A-1	2	2.12	70	70	10	19.6	224	96.0	1.18	7.30	2.14

C<sub>2</sub> added = ethylene added in the reactor with 1-buteneC<sub>2</sub> feed = ethylene feed during the polymerization

## CLAIMS

1. A process for polymerizing 1-butene comprising the step of contacting under polymerization conditions 1-butene and optionally from 0 to 20% by mol of ethylene, propylene and/or an alpha olefins of formula  $\text{CH}_2=\text{CHZ}$  wherein Z is a  $\text{C}_3\text{-C}_{10}$  alkyl group, in the presence of a catalyst system obtainable by contacting:

- a) a racemic or racemic-like bridged metallocene compound of formula (I)



wherein

$\text{R}^1$ , same or different, is hydrogen, a linear or branched saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl,  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

A, same or different, is a carbon atom, a germanium atom or a silicon atom; with the proviso that when m is 1 A is different from a carbon atom;

m is 1 or 2;

$\text{R}^2$ , same or different, is hydrogen, a linear or branched saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl,  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

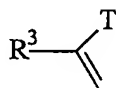
M is a transition metal atom selected from those belonging to group 4 of the Periodic Table of the Elements (new IUPAC version);

X, same or different, is a hydrogen atom, a halogen atom, or a R, OR,  $\text{OSO}_2\text{CF}_3$ ,

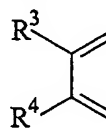
OCOR, SR,  $\text{NR}_2$  or  $\text{PR}_2$  group, wherein R is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_3\text{-C}_{20}$  cycloalkyl,  $\text{C}_6\text{-C}_{20}$  aryl,  $\text{C}_7\text{-C}_{20}$  alkylaryl or  $\text{C}_7\text{-C}_{20}$

arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a  $OR^{11}O$  group wherein  $R^{11}$  is a divalent radical selected from  $C_1$ - $C_{20}$  alkylidene,  $C_6$ - $C_{40}$  arylidene,  $C_7$ - $C_{40}$  alkylarylidene and  $C_7$ - $C_{40}$  arylalkylidene radicals;

L, same or different, is a moiety of formula (IIa) or (IIb)



(IIa)



(IIb)

wherein

in the moiety of formula (IIa) T bonds to the cyclopentadienyl group in position 5;

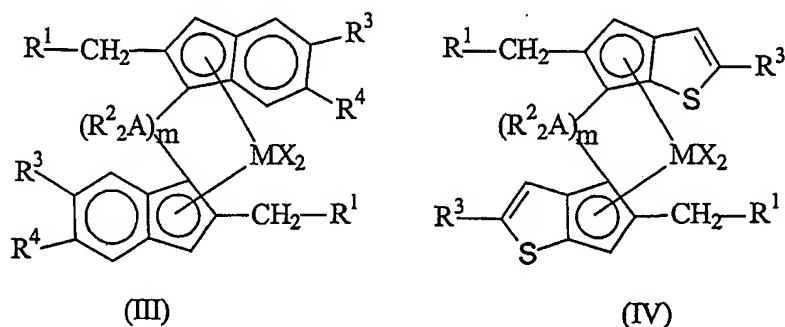
T is an oxygen (O) atom, a sulphur (S) atom or a  $CH_2$  group;

$R^3$  and  $R^4$  same or different are hydrogen, linear or branched saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl,  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or  $R^3$  and  $R^4$  form together a saturated or unsaturated condensed 5 or 6 membered ring optionally containing heteroatoms belonging to groups 13-16 of the Periodic Table of the Elements;

- b) an alumoxane or a compound able to form an alkylmetallocene cation; and
  - c) optionally an organo aluminum compound.
2. The process according to claim 1 wherein in the bridged metallocene compound of formula (I):
    - $R^1$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$ -alkyl radical;  $R^2$  is selected from hydrogen  $C_1$ - $C_{20}$ -alkyl or  $C_6$ - $C_{20}$ -aryl; m is 1; A is a silicon atom; M is zirconium or hafnium; X is halogen, a group R or OR;
  3. The process according to claim 2 wherein the bridge  $(R^2_2A)_m$  is  $Si(CH_3)_2$ ,  $SiPh_2$ ,  $CH_2CH_2$ ;
  4. The process according to anyone of claims 1 to 3 wherein in the moiety of formula (IIa)  $R^3$

is hydrogen or methyl.

5. The process according to anyone of claims 1 to 3 wherein in the moiety of formula (IIb)  $R^3$  and  $R^4$  are hydrogen or methyl.
6. The process according to anyone of claims 1 to 5 wherein the bridged metallocene compounds has formula (III) or (IV):



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , A, M, X and m have the meaning reported in claim 1.

7. A 1-butene homopolymer having the following characteristics:
  - intrinsic viscosity (I.V.)  $> 1$ ;
  - molecular weight distribution ( $M_w/M_n$ )  $< 3$ ;
  - isotactic triads (mm)  $>$  syndiotactic triads (rr);
  - 4,1 insertions  $< 0.35\%$ .
8. A 1-butene homopolymer according to claim 7 containing 4,1 insertions.
9. A 1-butene homopolymer according to claims 7-8 wherein the isotactic triads (mm) are higher than 97%.
10. A 1-butene homopolymer having the following characteristics:
  - intrinsic viscosity (I.V.)  $> 1$  dL/g;
  - flexural modulus (ASTM D 638)  $< 200\%$ ;
  - 4,1 insertions  $< 0.35\%$ .
11. The 1-butene homopolymer according to claim 10 containing 4,1 insertions.

## INTERNATIONAL SEARCH REPORT

Internat application No  
PCT/EP 02/06574

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F10/08 C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NAGA N ET AL: "POLYMERIZATION BEHAVIOR OF A-OLEFINS WITH RAC- AND MESO-TYPE ANSA-METALLOCENE CATALYSTS: EFFECTS OF COCATALYST AND METALLOCENE LIGAND" MACROMOLECULAR CHEMISTRY AND PHYSICS, WILEY VCH, WEINHEIM, DE, vol. 200, no. 7, July 1999 (1999-07), pages 1587-1594, XP000866730 ISSN: 1022-1352 page 1593  --- -/--	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

28 October 2002

Date of mailing of the international search report

13/11/2002

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## INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/EP 02/06574

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUHM, J. ET AL.: "Influence of metallocene structures on ethene copolymerization with 1-butene and 1-octene" JOURNAL OF MOLECULAR CATALYSIS, vol. 128, 1998, pages 215-227, XP002218351 page 222; tables 3,4 page 220, catalyst MI ---	1-11
X	EP 0 982 328 A (TOKUYAMA CORP). 1 March 2000 (2000-03-01) example 8 ---	1-6
X	US 4 298 722 A (COLLETTE JOHN W ET AL) 3 November 1981 (1981-11-03) column 9 -column 10; table 3 ---	7-11
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1991-203118 XP002215803 -& JP 03 126704 A (IDEMITSU PETROCHEM), 29 May 1991 (1991-05-29) abstract ---	7-11
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1986-044999 XP002215804 -& JP 60 262804 A (MITSUI PETROCHEM), 26 December 1985 (1985-12-26) abstract ---	7-11
X	ROSSI A ET AL: "END GROUPS IN 1-BUTENE POLYMERIZATION VIA METHYLALUMINOXANE AND ZIRCONOCENE CATALYST" MACROMOLECULES, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 28, no. 6, 13 March 1995 (1995-03-13), pages 1739-1749, XP000494862 ISSN: 0024-9297 cited in the application page 1744 --- -/--	7-9

## INTERNATIONAL SEARCH REPORT

Internati Application No

PCT/EP 02/06574

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NAGA N ET AL: "EFFECT OF CO-CATALYST SYSTEM ON ALPHA-OLEFIN POLYMERIZATION WITH RAC-AND MESO-UDIMETHYLSILYLENEBIS(2,3,5-TRIMETHYL-CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDE" MACROMOLECULAR: RAPID COMMUNICATIONS, WILEY VCH, WEINHEIM, DE, vol. 18, no. 7, 1 July 1997 (1997-07-01), pages 581-589, XP000698027 ISSN: 1022-1336 cited in the application page 585 -page 586; examples 9-11; tables 2,3	7-9
X	BUSICO V. ET AL.: "Regiospecificity of 1-butene polymerization catalyzed by C2-symmetric group IV metallocenes" MACROMOL. RAPID COMMUN., vol. 16, 1995, pages 269-274, XP001107140 cited in the application page 271 -page 272	7-11
X	WO 92 05208 A (EXXON CHEMICAL PATENTS INC) 2 April 1992 (1992-04-02) example 3	7-9
X	GB 1 460 795 A (HUELS CHEMISCHE WERKE AG) 6 January 1977 (1977-01-06) examples 1-6	10,11

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat

Application No

PCT/EP 02/06574

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0982328	A	01-03-2000	EP 0982328 A1	01-03-2000
			JP 2000239462 A	05-09-2000
			US 6268063 B1	31-07-2001
US 4298722	A	03-11-1981	NONE	
JP 3126704	A	29-05-1991	NONE	
JP 60262804	A	26-12-1985	JP 1849211 C	07-06-1994
			JP 5059922 B	01-09-1993
WO 9205208	A	02-04-1992	AT 134658 T	15-03-1996
			AU 8852591 A	15-04-1992
			DE 69117520 D1	04-04-1996
			DE 69117520 T2	01-08-1996
			EP 0548274 A1	30-06-1993
			ES 2084187 T3	01-05-1996
			JP 6501047 T	27-01-1994
			WO 9205208 A1	02-04-1992
GB 1460795	A	06-01-1977	DE 2318901 A1	07-11-1974
			FR 2225448 A1	08-11-1974
			IT 1004223 B	10-07-1976
			JP 1118651 C	28-10-1982
			JP 50009684 A	31-01-1975
			JP 57009365 B	20-02-1982
			US 4048419 A	13-09-1977